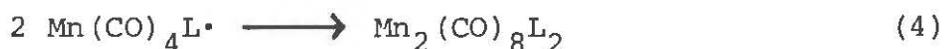
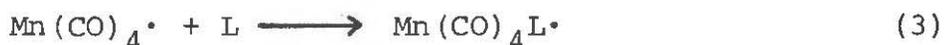
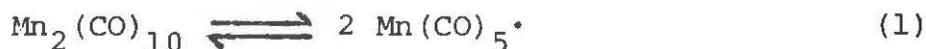


Flash Photolysis Studies  
of Dinuclear Transition Metal Carbonyl Compounds

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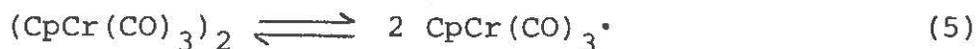
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Dinuclear transition metal carbonyl compounds possess an intense absorption ( $\epsilon \sim 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) in the 300-500 nm region of their UV-VIS spectra. Gray and co-workers determined that this absorption is polarized along the metal-metal axis and assigned this band to the  $\sigma \rightarrow \sigma^*$  transition [1]. Irradiation at wavelengths in the  $\sigma \rightarrow \sigma^*$  region results in a change in the metal-metal bond order from one to zero, generating radicals in solution. Kidd and Brown studied the photochemical reaction of  $\text{Mn}_2(\text{CO})_{10}$  with phosphine, L, and found  $\text{Mn}_2(\text{CO})_8\text{L}_2$  to be the major product [2]. Since the quantum yield of disappearance,  $\Phi_d$ , of the reaction is independent of the concentration and the nature of the phosphine, they proposed that substitution most likely occurs by dissociative loss of CO from  $\text{Mn}(\text{CO})_5^\cdot$ , followed by rapid reaction with phosphine (Steps 2 and 3):



Other reactions, including thermal substitution of phosphine onto transition metal hydrides [3,4] and the thermal decomposition of  $\text{HCo}(\text{CO})_4$  to  $\text{Co}_2(\text{CO})_8$  [5], are also thought to proceed via reactive unsubstituted radical centers. Brown and co-workers have studied the photochemical reaction of  $\text{Mn}_2(\text{CO})_8(\text{P}(\text{OC}_2\text{H}_5)_3)_2$  with  $\text{P}(\text{n-C}_4\text{H}_9)_3$  [2].  $\text{Mn}_2(\text{CO})_8(\text{P}(\text{n-C}_4\text{H}_9)_3)_2$  was the major product. The  $\Phi_d$  increased with increasing concentrations of  $\text{P}(\text{n-C}_4\text{H}_9)_3$ . Associative attack of  $\text{P}(\text{n-C}_4\text{H}_9)_3$  on the monosubstituted radical,  $\text{Mn}(\text{CO})_4(\text{P}(\text{OC}_2\text{H}_5)_3)^\cdot$ , was proposed as an intermediate step in the reaction. Hence, the mechanism of substitution onto a transition metal carbonyl radical may vary, depending upon the extent of substitution and/or which ligand is being substituted, CO or L.

Steric factors influence the strength of the metal-metal bond in transition metal carbonyl dimers and in the extreme cases prevent recombination of the radical species. Cotton and co-workers have found  $(\text{CpCr}(\text{CO})_3)_2$  in solution to be in equilibrium with its corresponding monomer [6]:



The following year Muetterties reported that  $((\eta^3\text{-C}_3\text{H}_5)\text{Fe}(\text{CO})_2\text{L})_2$  dissociated in solution to generate  $(\eta^3\text{-C}_3\text{H}_5)\text{Fe}(\text{CO})_2\text{L}^\bullet$  [7]. In the case where L is the bulky phosphine,  $\text{PPh}_3$ , there is no evidence for the dinuclear compound in solution. Most recently, Brown and co-workers have reported the synthesis of several persistent disubstituted manganese (0) radicals,  $\text{Mn}(\text{CO})_3\text{L}_2^\bullet$  ( $\text{L} = \text{P}(\text{n-C}_4\text{H}_9)_3$ ,  $\text{P}(\text{O-iC}_3\text{H}_7)_3$ ,  $\text{P}(\text{OC}_2\text{H}_5)_3$ ,  $\text{P}(\text{i-C}_4\text{H}_9)_3$ ,  $\text{P}(\text{i-C}_3\text{H}_7)_3$ ) [8,9].

Flash photolysis has been used to investigate the substitution and steric properties of unsubstituted and monosubstituted transition metal radicals. This technique involves imparting a short pulse of light ( $\sim 150 \mu\text{sec}$ ) onto a solution containing a dinuclear compound, and then indirectly monitoring the radicals generated by the pulse via a detection system focused on the  $\sigma \rightarrow \sigma^*$  transition of the dinuclear compound. The radical species do not absorb in this region. Flash photolysis has been performed on hexane solutions of  $\text{Mn}_2(\text{CO})_{10}$  and  $\text{Re}_2(\text{CO})_{10}$ . Under 1 atm CO pressure, the dinuclear species absorbance returns to the original value in accordance with a simple bimolecular rate law. Hence, bimolecular recombination of the  $\text{M}(\text{CO})_5^\bullet$  radicals is most likely the major process occurring in the solution. The unsubstituted radical recombination rate is near the diffusion-controlled limit. Without an initial CO concentration, an entirely different result is obtained. Intermediates are formed which are more strongly absorbing in the 350-500 nm region than the  $\text{M}_2(\text{CO})_{10}$  compounds.  $\text{M}_2(\text{CO})_8$  and  $\text{M}_2(\text{CO})_9$  are proposed as these intermediates. Their formation would result from the thermal loss of CO from  $\text{M}(\text{CO})_5^\bullet$  to generate  $\text{M}(\text{CO})_4^\bullet$ , which would either react with itself or  $\text{M}(\text{CO})_5^\bullet$  to form  $\text{M}_2(\text{CO})_8$  and  $\text{M}_2(\text{CO})_9$  respectively. Computer modeling of the kinetics supports this scheme. Flash photolysis experiments were performed on the disubstituted dinuclear compounds,  $\text{Mn}_2(\text{CO})_8\text{L}_2$  ( $\text{L} = \text{P}(\text{CH}_3)_3$ ,  $\text{P}(\text{n-C}_4\text{H}_9)_3$ ,  $\text{P}(\text{i-C}_4\text{H}_9)_3$ ,  $\text{P}(\text{i-C}_3\text{H}_7)_3$ ,  $\text{P}(\text{OPh})_3$ ,  $\text{PPh}_3$ ). With an initial CO concentration, the change in absorbance immediately after flashing followed second order kinetics, indicating sample recombination of the radicals was the major process occurring. The rate of recombination was found to decrease with increasing size of the phosphine ligand. The electronic properties of the phosphine ligand appear to have a negligible effect on the rate of radical recombination. Computer modeling enabled an upper limit to be placed on the rate of phosphine dissociation from  $\text{Mn}(\text{CO})_4\text{L}^\bullet$ . Without an initial CO concentration, a strongly absorbing intermediate is formed upon photolyzing  $\text{Mn}_2(\text{CO})_8\text{L}_2$  (analogous to  $\text{M}_2(\text{CO})_{10}$ ), even with an initial L concentration. This suggests that CO dissociates from  $\text{Mn}(\text{CO})_4\text{L}^\bullet$ .

### References

1. Levenson, R. A.; Gray, H. B.; Caesar, G. P. J. Am. Chem. Soc. 1970, 92, 3653.
2. Kidd, D. R.; Brown, T. L. J. Am. Chem. Soc. 1978, 100, 4095.
3. Hoffman, N. W.; Brown, T. L. Inorg. Chem. 1978, 17, 613.
4. Byers, B. H.; Brown, T. L. J. Am. Chem. Soc. 1977, 99, 2527.

5. Wegman, R. W.; Brown, T. L. J. Am. Chem. Soc. 1980, 102, 2494.
6. Adams, R. D.; Collins, D. E.; Cotton, A. J. J. Am. Chem. Soc. 1974, 96, 749.
7. Muetterties, E. L.; Sopinsky, B. A.; Zamaraev, K. I. J. Am. Chem. Soc. 1975, 97, 5299.
8. Kidd, D. R.; Cheng, C. P.; Brown, T. L. J. Am. Chem. Soc. 1978, 100, 4103.
9. McCullen, S. B., Ph.D. dissertation, University of Illinois; Urbana, Illinois; 1981.